Corrections of order $\alpha^4 R_\infty$ to the positronium P levels

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Corrections of order $\alpha^4 R_\infty$ to the positronium P levels are found. The calculation is reduced to ordinary perturbation theory for the nonrelativistic Schrödinger equation. The perturbation operators have Breit structure and are obtained by calculating the scattering amplitudes of nonrelativistic particles. The resulting energy corrections are $\delta E(2^1P_1)=0.06$ MHz, $\delta E(2^3P_2)=0.08$ MHz, $\delta E(2^3P_1)=0.025$ MHz, $\delta E(2^3P_0)=-0.58$ MHz.

1. INTRODUCTION

High-precision measurements of positronium structure provide a unique test of quantum electrodynamics. The typical accuracy reached in the measurements of the positronium 2^3S_1–$2^3P_J(J=0,1,2)$, 1^3S_1–2^3S_1 and 2^3S_1–2^1P_1 intervals is a few MHz (Refs. 1–6).[1)] The corrections of order $\alpha^4 R_\infty$ ($R_\infty=109\,737.315\,682\,7(48)$ cm^{-1} is the Rydberg constant)[7–9] are insufficient now for the comparison of quantum electrodynamics with those experimental data.

The two-body bound state QED problem is certainly of independent theoretical interest. The generally accepted theoretical approach to it goes back to Refs. 10–12. This approach starts from the introduction of a relativistic two-body wave equation, which can be solved exactly and in the nonrelativistic limit reduces to the Schrödinger equation. Then a perturbation series is developed about the exact solution.

Our approach is different. Its application to the corrections which are logarithmic in α is described in Refs. 13–15. The corrections discussed in Refs 13–15 and here are of relativistic origin and can be found as follows. We construct effective perturbation operators from the scattering amplitudes for nonrelativistic particles diagrams and then use those operators in the standard perturbation theory for the nonrelativistic Schrödinger equation.

The corrections of order $\alpha^4\log(1/\alpha)R_\infty$ to the positronium levels were calculated recently by Fell[16] and then by us (in Ref. 15 we have corrected a numerical error made in Ref. 14). This shift exists in the S states only and varies with the principal quantum number n as n^{-3}. The logarithmic structure of this correction allows one to treat the relativistic effects as a perturbation when deriving the result. However, if one tries to go beyond the logarithmic approximation, the logarithmic integrals which are cut off at the electron mass $1/m$ should be treated exactly, and the problem becomes extremely involved.

Fortunately, for states of higher angular momenta, $L>0$, the situation is better since their nonrelativistic wave functions fall off at small distances. Therefore, the integrals arising in the perturbation theory converge in the nonrelativistic region, which makes the problem quite tractable. The main difficulty (which we underestimated at the beginning of the work) is in the "book keeping."

Here we present the results of our analytical calculations for the corrections of order $\alpha^4 R_\infty$ to the positronium P levels. In the case $n=2$ the results for the fine-splitting of P levels can be directly compared with the data extracted from the experimental results of Refs 2, 5, and 6.

Similar corrections for the electron-electron interaction in helium were obtained numerically in Ref. 17.

2. CONTRIBUTIONS OF IRREDUCIBLE OPERATORS

We start with the kinematic correction resulting from averaging the second-order term in the dispersion law for electrons and positrons

$$\sqrt{m^2+p^2}-m=\frac{p^2}{2m}-\frac{p^4}{8m^3}+\frac{p^6}{16m^5}+\dots, \tag{1}$$

$$E^{(1)}_{\rm kin}=2\left\langle\frac{p^6}{16m^5}\right\rangle. \tag{2}$$

Using the equations of motion we find

$$E^{(1)}_{\rm kin}=\frac{m\alpha^6}{64}\left\langle\left(\mathscr{E}_n+\frac{1}{r}\right)\frac{p^2}{2}\left(\mathscr{E}_n+\frac{1}{r}\right)\right\rangle$$

$$=\frac{m\alpha^6}{64}\left\langle\mathscr{E}_n^3+\frac{3\mathscr{E}_n^2}{r}+\frac{3\mathscr{E}_n}{r^2}+\frac{1}{r^3}+\frac{1}{2r^4}\right\rangle,$$

$$\mathscr{E}_n\equiv\frac{2E_n}{m\alpha^2}=-\frac{1}{2n^2}. \tag{3}$$

The substitution of the nonrelativistic Coulomb expectation values for $1/r^k$,

$$\langle r^{-1}\rangle=\frac{1}{n^2},\quad \langle r^{-2}\rangle=\frac{2}{3n^3}, \tag{4}$$

$$\langle r^{-3}\rangle=\frac{1}{3n^3},\quad \langle r^{-4}\rangle=\frac{2}{5n^3}\left(1-\frac{2}{3n^2}\right), \tag{5}$$

reduces this energy correction to

$$E^{(1)}_{\rm kin}=\frac{\varepsilon_n}{2^6\cdot 3\cdot 5}\left(8-\frac{17}{n^2}+\frac{75}{8n^3}\right), \tag{6}$$

where $\varepsilon_n\equiv m\alpha^6/n^3$.

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2.1 Relativistic corrections to the Coulomb interaction

This perturbation operator will be extracted from the scattering amplitude for free particles. It is convenient to consider the positron as an electron of positive charge. Then the scattering amplitude due to the single Coulomb exchange is

$$A_C=-\frac{4\pi\alpha}{q^2}\rho(\mathbf{p}',\mathbf{p})\rho(-\mathbf{p}',-\mathbf{p}), \tag{7}$$

where

$$\rho(\mathbf{p}',\mathbf{p})=u^+(\mathbf{p}')u(\mathbf{p}),\quad \mathbf{q}=\mathbf{p}'-\mathbf{p}. \tag{8}$$

We substitute into (7) the solution of the free-particle Dirac equation

$$u(\mathbf{p})=\sqrt{\frac{2\omega_\mathbf{p}}{\omega_\mathbf{p}+m}}\lambda_+(\mathbf{p})w, \tag{9}$$

where w is a bispinor describing a particle at rest,

$$\lambda_+(\mathbf{p})=\frac{1}{2}\left(1+\frac{\alpha\mathbf{p}+\beta m}{\omega_\mathbf{p}}\right),\quad \omega_\mathbf{p}=\sqrt{p^2+m^2}. \tag{10}$$

The corrections of fourth order in v/c are

$$V_C=-\frac{\alpha}{16m^4}\frac{4\pi}{q^2}\{(p'^2-p^2)^2-i(\mathbf{S},[\mathbf{p}'\mathbf{p}])$$
$$\times(q^2+3p'^2+3p^2)-2(\mathbf{S},[\mathbf{p}'\mathbf{p}])^2\}. \tag{11}$$

We have neglected here the operator proportional to $p^2+p'^2$ since its expectation value in the coordinate representation $\langle\delta(\mathbf{r})\Delta+\Delta\delta(\mathbf{r})\rangle$ vanishes for P states. The expectation value of the operator (11) is again conveniently calculated in the coordinate representation. Its spin-independent part is

$$\left\langle\frac{4\pi}{q^2}(p'^2-p^2)^2\right\rangle=\left\langle\left[p^2,\left[p^2,\frac{1}{r}\right]\right]\right\rangle$$
$$=2\left\langle\left[\frac{1}{r},\left[p^2,\frac{1}{r}\right]\right]\right\rangle=4\langle r^{-4}\rangle. \tag{12}$$

The treatment of the spin-dependent operators is somewhat more complicated. We go over to the Fourier transforms of the operators:

$$\int\frac{d^3q}{(2\pi)^3}\frac{4\pi\mathbf{q}}{q^2}e^{i\mathbf{qr}}=\frac{i\mathbf{n}}{r^2}, \tag{13}$$

$$\int\frac{d^3q}{(2\pi)^3}\frac{4\pi q_iq_j}{q^2}e^{i\mathbf{qr}}=\frac{\delta_{ij}-3n_in_j}{r^3}+4\pi n_in_j\delta(\mathbf{r}), \tag{14}$$

then use the equations of motions and the expectation values (4), as well as the value of the radial wave function derivative at the origin

$$|R'_{n1}(0)|^2=\frac{4}{9n^2}\left(1-\frac{1}{n^2}\right). \tag{15}$$

In this way we get

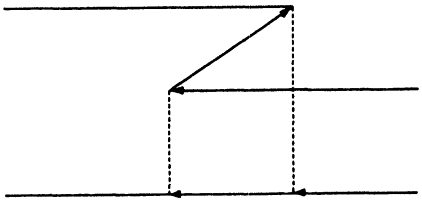

FIG. 1. Z-type double-Coulomb exchange.

$$E_C^{(1)}=\frac{\varepsilon_n}{2^6\cdot 5^2}\left\{-5\left(1-\frac{2}{3n^2}\right)-\mathbf{SL}\left(19-\frac{121}{6n^2}\right)\right.$$
$$\left.+\frac{(\mathbf{SL})^2+\mathbf{S}^2}{3}\left(1-\frac{3}{2n^2}\right)\right\}. \tag{16}$$

Now, because of the Coulomb interaction the electron (positron) can go over to a negative-energy intermediate state. The corresponding contributions are described by Z-diagrams of the kind presented in Fig. 1. Here the particle staying in a positive-energy state can be treated in the nonrelativistic approximation. Specifically, the large energy denominator, equal approximately to $2m\gg E_n$, due to "heavy" intermediate states, and the small matrix element (which vanishes in the nonrelativistic limit) of the Z-line make the power of α in the perturbation sufficiently large. In this way we get for the perturbation operator

$$V_{C-}=\frac{(4\pi\alpha)^2}{2m}\int\frac{d^3k}{(2\pi)^3}\frac{1}{k^2(\mathbf{k}-\mathbf{q})^2}\times\left(\frac{1}{2}\left(1-\frac{m}{\omega_{\mathbf{p}+\mathbf{k}}}\right.\right.$$
$$\left.\left.+\frac{\sigma\mathbf{p}'}{2m}\frac{\sigma\mathbf{p}}{2m}-\frac{\sigma\mathbf{p}'}{2m}\frac{\sigma(\mathbf{p}+\mathbf{k})}{2m}-\frac{\sigma(\mathbf{p}+\mathbf{k})}{2m}\frac{\sigma\mathbf{p}}{2m}\right)\right)$$
$$\to-\frac{(4\pi\alpha)^2}{(2m)^3}\int\frac{d^3k}{(2\pi)^3}\frac{\mathbf{k}(\mathbf{q}-\mathbf{k})}{k^2(\mathbf{q}-\mathbf{k})^2}. \tag{17}$$

Going over to the coordinate representation, we note that the last integral is in fact the convolution of the Fourier-transform of the operator $i\mathbf{n}/r^2$ with itself. So,

$$E_{C-}^{(1)}=\frac{m\alpha^6}{2^6}\langle r^{-4}\rangle=\frac{\varepsilon_n}{2^5\cdot 5}\left(1-\frac{2}{3n^2}\right). \tag{18}$$

Note that the integral in (17) formally diverges at large k. It can be easily seen, however, that the divergent part is independent of the momentum transfer $\mathbf{q}$. Therefore in the coordinate representation the corresponding operator is just $\delta(\mathbf{r})$. Its expectation value is nonvanishing only in S states, where it can be shown to contribute (by accurately cutting off the linear divergence at $k\sim m$) a correction of the order $m\alpha^5$.

2.2 Single magnetic exchange

In the noncovariant perturbation theory the electron-positron scattering amplitude due to exchange of one magnetic quantum is

$$A_M=-\frac{4\pi\alpha}{q}\frac{j_i(\mathbf{p}',\mathbf{p})j_j(-\mathbf{p}',-\mathbf{p})}{E_n-q-(p^2+p'^2)/2m}\left(\delta_{ij}-\frac{q_iq_j}{q^2}\right). \tag{19}$$

Here

$$\mathbf{j}(\mathbf{p}',\mathbf{p})=u^{+}(\mathbf{p}')\alpha u(\mathbf{p}) \tag{20}$$

is the matrix element of the current taken over the solutions (9) of the free Dirac equation. In the dispersion law for the electron and positron the nonrelativistic approximation suffices.

We start from the contribution to the perturbation operator produced by the v^2/c^2 corrections to the currents:

$$V_{\text{curr}}=\frac{\alpha}{4m^4}\frac{4\pi}{q^2}\left\{4p'^2\left(p^2-\frac{(\mathbf{pq})^2}{q^2}+\mathbf{pq}\frac{i([\mathbf{qp}]\mathbf{S})}{q^2}+\frac{1}{2}\right.\right.$$
$$\left.\times(\mathbf{qS})^2\right)+\frac{p'^2-p^2}{2}\left((p'^2-p^2)1+\frac{i([\mathbf{qp}],\mathbf{S})}{q^2}\right.$$
$$\left.\left.-\mathbf{S}^2\right)+(2\mathbf{p}+\mathbf{q})\mathbf{S}(\mathbf{qS})\right)]. \tag{21}$$

Here we have again neglected the terms with vanishing P-state expectation values. Going over to the coordinate representation by means of (13), (14) and

$$\int\frac{d^3q}{(2\pi)^3}\frac{4\pi q_iq_j}{q^4}e^{i\mathbf{qr}}=\frac{\delta_{ij}-n_in_j}{2r}, \tag{22}$$

$$\int\frac{d^3q}{(2\pi)^3}\frac{4\pi\mathbf{q}}{q^4}e^{i\mathbf{qr}}=\frac{i\mathbf{n}}{2}, \tag{23}$$

we obtain

$$E^{(1)}_{\text{curr}}=\frac{\varepsilon_n}{2^5\cdot 5}\left\{\frac{17}{3}-\frac{11}{n^2}+\frac{5}{n^3}-\frac{7\mathbf{SL}}{2}\left(1-\frac{1}{n^2}\right)+2(\mathbf{SL})^2\left(1\right.\right.$$
$$\left.\left.-\frac{7}{6n^2}\right)-2\mathbf{S}^2\left(1-\frac{1}{n^2}\right)\right\}. \tag{24}$$

Let us consider now the retardation effect. To this end the currents can be taken in the leading approximation:

$$\mathbf{j}(\mathbf{p}',\mathbf{p})\rightarrow\frac{1}{2m}(\mathbf{p}'+\mathbf{p}+i[\mathbf{q}\sigma]). \tag{25}$$

For momentum transfer on the atomic scale, $q\sim m\alpha$, the perturbation of interest originates from the second-order term in the expansion of the factor $[E_n-(p^2+p'^2)/2m-q]^{-1}$ in (19) in powers of $(E_n-(p^2+p'^2)/2m)/q$:

$$V_{\text{ret}}=-\frac{\alpha}{2m^2}\frac{4\pi}{q^2}\frac{(E_n-(p^2+p'^2)/2m)^2}{q^2}\left\{q^2+2\mathbf{pp}'\right.$$
$$\left.-2\frac{(\mathbf{qp}')(\mathbf{qp})}{q^2}-2i[\mathbf{pq}],\mathbf{S}\right)-q^2\mathbf{S}^2+(\mathbf{qS})^2\}. \tag{26}$$

At first sight, the expectation value of this operator diverges linearly at small q. This divergence can be demonstrated however to be unrelated to the order-$m\alpha^6$ correction we are interested in. Indeed, let us split the integration over q into two regions, from 0 to λ and from λ to ∞ where $m\alpha^2\ll\lambda\ll m\alpha$. In the second region our expansion is applicable and the result of integration contains a term proportional to $1/\lambda$. Since the initial integral is independent of λ, this term cancels in the sum with the integral over the first region calculated without expanding. On the other hand, this last integral has no contribution of the α^4R_∞ order independent of λ. Therefore, taking as the Fourier-transform of

$$\frac{4\pi}{q^4}\left(\mathbf{pp}'-\frac{(\mathbf{qp}')(\mathbf{qp})}{q^2}\right), \tag{27}$$

the operator

$$-\frac{r}{8}(3p^2-(\mathbf{np})^2), \tag{28}$$

we finally get

$$E^{(1)}_{\text{ret}}=\frac{\varepsilon_n}{2^5\cdot 3\cdot 5}\left(14-\frac{15}{n}+\frac{13}{2n^2}\right). \tag{29}$$

Since a magnetic quantum propagates for a finite time, it can cross arbitrary number of the Coulomb ones. Simple counting of the momentum powers demonstrates that it is sufficient to include diagrams with one and two Coulomb quanta (dashed lines) crossed by the magnetic photon (wavy line). In the first case, Fig. 2, the perturbation operator arises as a product of the Pauli currents (25) and the first-order term in the expansion in $(E_n-(p^2+p'^2)/2m)/q$:

$$V_{MC}=\frac{\alpha^2}{m^2}\int\frac{d^3k}{(2\pi)^3}\frac{(4\pi)^2}{k^4(\mathbf{q}-\mathbf{k})^2}\left(\frac{p^2+p'^2-\mathbf{qk}+k^2}{2m}-E_n\right)$$
$$\times\left\{k^2+2\mathbf{pp}'-2\frac{(\mathbf{kp}')(\mathbf{kp})}{k^2}-2i(\mathbf{pk},\mathbf{S})\right.$$
$$\left.-k^2\mathbf{S}^2+(\mathbf{kS})^2\right\}. \tag{30}$$

In the second case all the elements of the diagram in Fig. 3 should be taken to leading nonrelativistic approximation:

$$V_{MCC}=-\frac{\alpha^3}{2m^2}\int\frac{d^3k}{(2\pi)^3}\int\frac{d^3k'}{(2\pi)^3}\frac{(4\pi)^3}{k^4(\mathbf{q}-\mathbf{k}')^2(\mathbf{k}'-\mathbf{k})^2}$$
$$\times\left\{k^2+2\mathbf{pp}'-2\frac{(\mathbf{kp}')(\mathbf{kp})}{k^2}-2i([\mathbf{pk}],\mathbf{S})-k^2\mathbf{S}^2\right.$$
$$\left.+(\mathbf{kS})^2\right\}. \tag{31}$$

All the integrals in (30) and (31) are convolutions of the already known Fourier-transforms of powers of $\mathbf{r}$. In this way we get for the first operator:

$$E^{(1)}_{MC}=\frac{\varepsilon_n}{2^5\cdot 3\cdot 5}\left\{-13+\frac{30}{n}-\frac{13}{n^2}-\frac{3\mathbf{SL}}{5}\left(29+\frac{2}{3n^2}\right)\right.$$
$$\left.+2\frac{(\mathbf{SL})^2-4\mathbf{S}^2}{5}\left(13-\frac{2}{n^2}\right)\right\}; \tag{32}$$

and for the second one:

$$E^{(1)}_{MCC}=\frac{\varepsilon_n}{2^5\cdot 3\cdot 5}\left\{15\left(1-\frac{1}{n}\right)+9\mathbf{SL}-2(\mathbf{SL})^2+8\mathbf{S}^2\right\}. \tag{33}$$

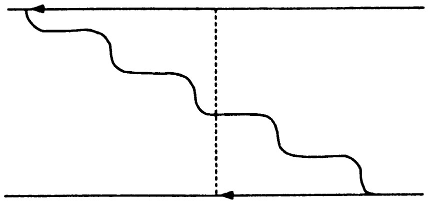

FIG. 2. Single-magnetic-single-Coulomb exchange.

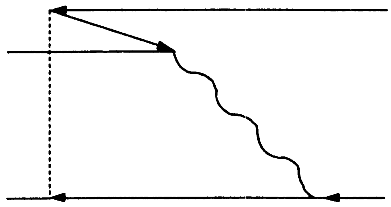

FIG. 4. Z-type single-magnetic-single-Coulomb exchange.

One more energy correction of order $\alpha^4 R_\infty$ associated with single magnetic exchange is due to Z-type diagrams (see Fig. 4). To leading approximation one gets easily

$$V_{M-}=\frac{\alpha^2}{m^3}\int\frac{d^3k}{(2\pi)^3}\frac{(4\pi)^2}{k^2(\mathbf{q}-\mathbf{k})^2}\{\mathbf{k}(\mathbf{q}-\mathbf{k})(1-\mathbf{S}^2)+\mathbf{kS}(\mathbf{q}-\mathbf{k})\mathbf{S}+\tfrac{1}{2}i([\mathbf{kq}],\mathbf{S})\}. \tag{34}$$

Standard calculations give now

$$E^{(1)}_{M-}=-\frac{\varepsilon_n}{2^2\cdot 5^2}\left\{\frac{5}{2}+\frac{3}{4}\mathbf{SL}-(\mathbf{SL})^2-\mathbf{S}^2\right\}\left(1-\frac{2}{3n^2}\right). \tag{35}$$

2.3 True radiative corrections

Curiously enough, even the true radiative corrections of order $\alpha^4 R_\infty$ to the P-level energy can be presented in a simple form practically without special calculation. They can be easily demonstrated to be confined here to anomalous magnetic moment contribution to the single magnetic exchange, i.e. to a trivial modification of the usual Breit Hamiltonian. With this contribution the Pauli current becomes

$$\mathbf{j}(\mathbf{p}',\mathbf{p})\rightarrow\frac{1}{2m}(\mathbf{p}'+\mathbf{p}+ig[\mathbf{q}\boldsymbol{\sigma}]), \tag{36}$$

where

$$g=1+\frac{\alpha}{2\pi}-c\left(\frac{\alpha}{\pi}\right)^2+\ldots,\quad c\approx 0.328. \tag{37}$$

It should be noted here that the anomalous magnetic moment contributions to the first-order retardation effect and to the diagram in Fig. 2 cancel. This corresponds to the absence of corrections of order v/c to the Breit magnetic exchange. In this way we get the following correction to the P-level energy:

$$E^{(1)}_{\mathrm{rad}}=-\frac{\varepsilon_n}{2^4\cdot 3\cdot 5}\frac{1}{\pi^2}\left\{\left(\frac{3}{4}+4c\right)\mathbf{SL}+(1-8c)\left(\frac{3}{2}(\mathbf{SL})^2-\mathbf{S}^2\right)\right\}. \tag{38}$$

Two of its features are noteworthy. First, it vanishes in singlet states, which looks rather natural. Second, it has an extra factor $1/\pi^2$ which reflects its radiative origin as distinct from the relativistic origin of other corrections of order $\alpha^4 R_\infty$ to P-levels.

2.4 Double magnetic exchange

Let us consider now irreducible diagrams with two magnetic quanta. In our approximation they are confined to the type presented in Fig. 5. Their sum reduces to

$$V_{MM}=\frac{\alpha^2}{m^3}\int\frac{d^3k}{(2\pi)^3}\frac{(4\pi)^2}{k^2k'^2}\left\{\mathbf{pp}'-2\frac{(\mathbf{kp})(\mathbf{kp}')}{k^2}+\frac{(\mathbf{kp})(\mathbf{kk}')(\mathbf{kp}')}{k^2k'^2}-\frac{\mathbf{kk}'}{2}+i\mathbf{S}\left([\mathbf{qp}]-[\mathbf{kp}]-\frac{[\mathbf{qk}](\mathbf{kp}')}{k^2}\right)\right\}, \tag{39}$$

where $\mathbf{k}'=\mathbf{q}-\mathbf{k}$. Now we substitute the products of operators in the coordinate representation for the convolutions of their Fourier-transforms and take the corresponding expectation values. In this way we get

$$E^{(1)}_{MM}=\frac{\varepsilon_n}{2^4\cdot 3\cdot 5}\left\{10\left(1-\frac{1}{n^2}\right)-3\mathbf{SL}\left(1-\frac{2}{3n^2}\right)\right\}. \tag{40}$$

3. CORRECTIONS OF SECOND ORDER IN THE BREIT HAMILTONIAN

The next class of corrections of order $\alpha^4 R_\infty$ originates from the iteration of the usual Breit Hamiltonian V to second order in v/c.

Before proceeding to the calculation, let us note that the Breit potential for the positronium (see, e.g., Ref. 18, Sec. 84),

$$V=-\frac{p^4}{4m^3}+\frac{\pi\alpha}{m^2}\delta(\mathbf{r})-\frac{\alpha}{2m^2r}[p^2+(\mathbf{np})^2]+\frac{3\alpha}{2m^2r^3}\mathbf{LS}+\frac{3\alpha}{2m^2r^3}\left\{(\mathbf{Sn})^2-\frac{1}{3}\mathbf{S}^2\right\}+\frac{\pi\alpha}{m^2}\left(\frac{7}{3}\mathbf{S}^2-2\right)\delta(\mathbf{r}), \tag{41}$$

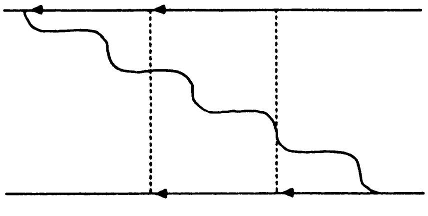

FIG. 3. Single-magnetic-double-Coulomb exchange.

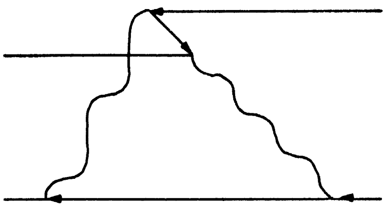

FIG. 5. Double-magnetic exchange.

has nonvanishing matrix elements for $|\Delta L|=0$, 2 only. The contribution of virtual F-levels will be found later. For now we average the angular dependence of (41) over the P-state wave function:

$$3(\mathbf{Sn})^2-\mathbf{S}^2\to-\tfrac{3}{5}\left(2(\mathbf{SL})^2+\mathbf{SL}-\tfrac{4}{3}\mathbf{S}^2\right). \tag{42}$$

After this procedure the perturbation (41) can be written as follows:

$$V\to\frac{m\alpha^4}{16}v, \tag{43}$$

$$v=\left(a\left\{h,\frac{1}{r}\right\}+b[h,ip_r]+c\frac{1}{r^2}\right), \tag{44}$$

where

$$a=-3,\quad b=1+\kappa,\quad c=-4+\kappa; \tag{45}$$

$$\kappa=\frac{6\mathbf{SL}-3(\mathbf{SL})^2+2\mathbf{S}^2}{5}; \tag{46}$$

$p_r=-i(\partial_r+1/r)$ is the radial momentum, while

$$h=\frac{p_r^2}{2}+\frac{1}{r^2}-\frac{1}{r}$$

is the unperturbed Hamiltonian for the radial motion with $L=1$ in the Coulomb field.

According to the standard rules,

$$E_P^{(2)}=\langle VGV\rangle=\frac{m\alpha^6}{128}\langle vgv\rangle, \tag{47}$$

$$G={\sum_k}'\frac{|kP\rangle\langle kP|}{E_n-E_k}=\frac{2}{m\alpha^2}g, \tag{48}$$

$$g={\sum_k}'\frac{|kP\rangle\langle kP|}{\mathcal{E}_n-\mathcal{E}_k}. \tag{49}$$

Since all relativistic effects are included here in the perturbation, the intermediate states $|kP\rangle$ are merely eigenfunctions of the nonrelativistic Schrödinger equation in the Coulomb field.

The representation (44) enables us to find the energy correction (47) without recourse to the exact form of the Coulomb Green's function g. Specifically,

$$\langle vgv\rangle=\frac{1}{2}\left\langle\left(2a\mathcal{E}_n\frac{1}{r}-a\left[h,\frac{1}{r}\right]+b[h,ip_r]+c\frac{1}{r^2}\right)gv+vg\left(2a\mathcal{E}_n\frac{1}{r}+a\left[h,\frac{1}{r}\right]+b[h,ip_r]+c\frac{1}{r^2}\right)\right\rangle, \tag{50}$$

where

$$\langle vgv\rangle=-a\mathcal{E}_n(2\langle v\rangle+\partial_\beta\langle v\rangle-\langle\partial_\beta v\rangle)-\frac{a}{2}\left\langle\left\{v,\frac{1}{r}\right\}\right\rangle+\frac{b}{2}\langle[ip_r,v]\rangle+c(\partial_\gamma\langle v\rangle-\langle\partial_\gamma v\rangle). \tag{51}$$

When passing from (50) to (51) we used the equation of motion and also the fact that perturbations in $1/r$ and $1/r^2$ result in variations of β and γ, respectively, in the modified Hamiltonian,

$$h(\beta,\gamma)=\frac{p_r^2}{2}+\frac{\gamma}{r^2}-\frac{\beta}{r}. \tag{52}$$

Derivatives in (51) are taken at $\beta=\gamma=1$.

Substituting (44) into (51) provides us with the expression containing just the mean values of $1/r^k$, $k=1,2,3,4$ [see (4)]. Equating to zero coefficients of the various powers of $1/n$ we obtain

$$E_P^{(2)}=\frac{m\alpha^6}{128n^3}\left\{-\frac{3a^2+14ab+13b^2}{15}-\frac{2c(2c+9a+9b)}{27}-\frac{2c^2}{3n}+\frac{2}{3n^2}\left(\frac{11a^2+13ab+6b^2}{5}+4ac\right)-\frac{5a^2}{2n^3}\right\}. \tag{53}$$

Finally, substituting the expressions for a, b, c (45), we get the contribution of intermediate P states to the iteration of the Breit Hamiltonian:

$$E_P^{(2)}=\varepsilon_n\left\{-\frac{1022-844\kappa+227\kappa^2}{2^7\cdot3^3\cdot5}-\frac{(4-\kappa)^2}{2^6\cdot3\cdot n}+\frac{102-29\kappa+2\kappa^2}{2^6\cdot5\cdot n^2}-\frac{45}{2^8\cdot n^3}\right\}. \tag{54}$$

Transitions to intermediate F states are induced by the operator $(\mathbf{Sn})^2$ contained in (41). Due to the conservation of the total angular momentum such transitions are possible in states with $J=2$ only. The matrix element squared of the operator, $(\mathbf{Sn})^2$, is easily calculated by the closure condition:

$$\begin{aligned}|\langle P_2|(\mathbf{Sn})^2|F_2\rangle|^2&=\langle P_2|(\mathbf{Sn})^4|P_2\rangle-\langle P_2|(\mathbf{Sn})^2|P_2\rangle^2\\&=\langle P_2|(\mathbf{Sn})^2|P_2\rangle-\langle P_2|(\mathbf{Sn})^2|P_2\rangle^2\\&=\frac{6}{25}.\end{aligned} \tag{55}$$

We have used here the identity $(\mathbf{Sn})^3|P\rangle=\mathbf{Sn}|P\rangle$.

To calculate the radial part of the correction, proportional to

TABLE I. Fine-structure intervals between $2^{2S+1}P_J$ levels (in MHz).

	Experiments		Theory	
Transitions	Michigan[2,5]	Mainz[6]	Total	$R_\infty\alpha^4$ contribution
$E(^3P_2)-E(^3P_0)$	9884.5 ± 10.5	9875.27 ± 4.44	9871.54	0.66
$E(^3P_1)-E(^3P_0)$	5502.8 ± 10.9	5487.23 ± 4.50	5485.84	0.60
$E(^1P_1)-E(^3P_0)$	7323.1 ± 16.5	7319.65 ± 7.64	7312.88	0.64

$$\left\langle\frac{1}{r^3}\sum_k\frac{|kF\rangle\langle kF|}{\mathscr{E}_n-\mathscr{E}_k}\frac{1}{r^3}\right\rangle, \tag{56}$$

we represent the operator $1/r^3$ in the form

$$\frac{1}{r^3}=\frac{1}{18}\left[h\left(-ip_r-\frac{5}{r}+\frac{1}{5}\right)-\left(-ip_r-\frac{5}{r}+\frac{1}{5}\right)h_F\right] \tag{57}$$

$$=\frac{1}{18}\left[h_F\left(-ip_r+\frac{5}{r}-\frac{1}{5}\right)-\left(-ip_r+\frac{5}{r}-\frac{1}{5}\right)h\right], \tag{58}$$

where

$$h_F=\frac{p_r^2}{2}+\frac{6}{r^2}-\frac{1}{r} \tag{59}$$

is the unperturbed Hamiltonian for the radial motion with $L=3$ in the Coulomb field. The energy correction is again expressed in terms of r:

$$E_F^{(2)}=m\alpha^6\frac{3}{2^8\cdot5^2}\left\langle\frac{2}{5r^3}-\frac{7}{r^4}\right\rangle=-\frac{\varepsilon_n}{2^6\cdot5^3}\left(10-\frac{7}{n^2}\right). \tag{60}$$

4. NUMERICAL RESULTS

Let us summarize the numerical values of the α^4R_∞ corrections to the energies of positronium $2P$ levels. They are

0.06 MHz for 2^1P_1,

0.08 MHz for 2^3P_2,

0.025 MHz for 2^3P_1,

-0.58 MHz for 2^3P_0.

We wish to emphasize here that the last correction is quite comparable in magnitude to the corresponding logarithmic correction (of order $\alpha^4\log\alpha\, R_\infty$) to the positronium $2S$-levels. The latter, for instance is 0.96 MHz for the 2^3S_1 state.[15,16] Therefore, there is no special reasons to expect that the nonlogarithmic corrections (of order α^4R_∞) to the positronium S levels are small. It makes their calculation a problem of considerable interest.

Including α^2R_∞ and α^3R_∞ terms we obtain the fine-structure intervals between $2^{2S+1}P_J$ levels. In Table I these theoretical values are compared with the transition frequencies taken from the results of two recent experiments[2,5,6] (all systematic and statistical errors are added quadratically when extracting the experimental numbers).

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